Synthesis, Fluorescence, and Photostabilities of 3-(Perfluoroalkyl)coumarins

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The regioselective reaction of coumarins **1** with bis(perfluoroalkanoyl) peroxides affords 3-(perfluoroalkyl)coumarins **2** in moderate yields. The absorption and emission maxima of coumarins **2** show bathochromic shifts compared with the 3-unsubstituted coumarins. The fluorescence intensities of 3-(perfluoroalkyl)coumarins **2** are smaller than those of the 3-unsubstituted ones. However, the photostabilities of coumarins **2** are higher than those of the 3-unsubstituted ones.

Much attention has been paid to the synthesis and characterization of organic fluorine compounds due to their unique properties. The introduction of halogen atoms and/or perfluoroalkyl groups into dye molecules is known to improve light fastness. However, only a few dyes bearing fluorine or a trifluoromethyl group have been synthesized, because of the limitation of the starting materials. Recently, the perfluoroalkylation of heteroaromatics using bis(heptafluorobutyryl) peroxides has been reported[1]. Though coumarins have been used as fluorescent and laser dyes, they are photochemically unstable. In order to improve the photostability, 3,4-disubstituted and 4-trifluoromethylated coumarins have been synthesized[2]. In our previous paper, the regioselective synthesis of 3-(perfluoroalkyl)coumarins has been reported[3]. In this paper we describe the synthesis, fluorescence, and photostability of 3-(perfluoroalkyl)coumarins.

Synthesis of 3-(Perfluoroalkyl)coumarins

Scheme 1 and Table 1 show the reaction of coumarin (**1a**) with bis(heptafluorobutyryl) peroxide. The highest yield of 3-(heptafluoropropyl)coumarin (**2a**) is obtained by using a 1:1 molar ratio of **1a** to peroxide at reflux temperature (runs 1 – 5). The reaction also affords polymerized products which are not separated by chromatography. When the reaction is carried out in the presence of air, the yield of **2a** is lowered, suggesting the formation of radical species derived from an electron-transfer process during the reaction (runs 3, 6)[1].

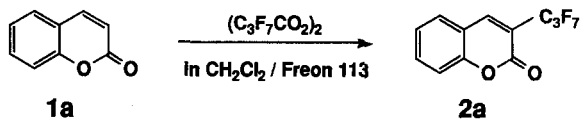
Scheme 2 and Table 2 show the synthesis of 3-(perfluoroalkyl)coumarins **2**. The reaction of coumarins **1** with bis(heptafluorobutyryl) peroxide gives the corresponding 3-(heptafluoropropyl)coumarins **2** in 15 – 67% yields (runs 1 – 6, 8, 9, 12 – 16, 19). No remarkable effects of 4- and 7-substituents on the formation of **2** except for **2g** are observed (run 7). In the case of **1g**, the formation of a small amount of 7-[(heptafluorobutyryl)amino]-4-methylcoumarin is confirmed by GC/MS analysis. Interestingly, the reaction of 7-amino-4-(trifluoromethyl)coumarin (**1l**) with the peroxide affords 3-(heptafluoropropyl)coumarin (**2l**) in 46% yield (run 14). In the reaction of bis(perfluoroalkanoyl) peroxides with amino derivatives the electron-transfer process, which provides the perfluoroalkyl derivatives, may compete with both the nucleophilic attack of the amino group on the perfluorocarboxylic acids produced during the reaction and polymerization process. The 4-trifluoromethyl group of **1l** may lower the nucleophilicity of the 7-amino nitrogen to suppress the nucleophilic reaction. The reactions of **1i** and **1n** with bis(trifluoroacetyl) and bis(pentadecafluorooctanoyl) peroxides furnish the corresponding 3-(perfluoroalkyl)-coumarins **2i'**, **2i''**, **2n'**, **2n''** in moderate yields (runs 10, 11, 17, 18). No reactions of 3-methyl- and 7-(diethylamino)-3-(1-methyl-2-benzimidazolyl)coumarins with bis(heptafluorobutyryl) peroxide are observed. In the perfluoroalkylation of 7-(diethylamino)-3-(heptafluoropropyl)-4-methylcoumarin (**2i**) most of the starting material is recovered.

Table 1. Reaction of coumarin (**1a**) with bis(heptafluorobutyryl) peroxide[a]

Run	1a mmol	Peroxide mmol	Gas phase	Temperature °C	1a[b] mmol	2a[b] mmol
1	1.00	1.00	Ar	0[c]	0.99	trace
2	1.00	1.00	Ar	20[c]	0.40	0.20
3	1.00	1.00	Ar	reflux[d]	trace	0.38
4	1.50	1.00	Ar	reflux[d]	0.51	0.21
5	2.00	1.00	Ar	reflux[d]	1.13	0.23
6	1.00	1.00	Air	reflux[d]	0.33	0.19

[a] Dichlormethane solution (20 ml) of **1a** treated with a 5.0% bis(heptafluorobutyryl) peroxide/Freon 113 solution (8.5 g, 1 mmol). – [b] Determined by GLC. – [c] Stirred for 8 h. – [d] Refluxed for 3 h.

Scheme 1



1a **2a**

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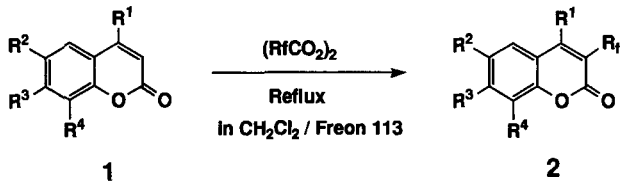
Scheme 2



1 2

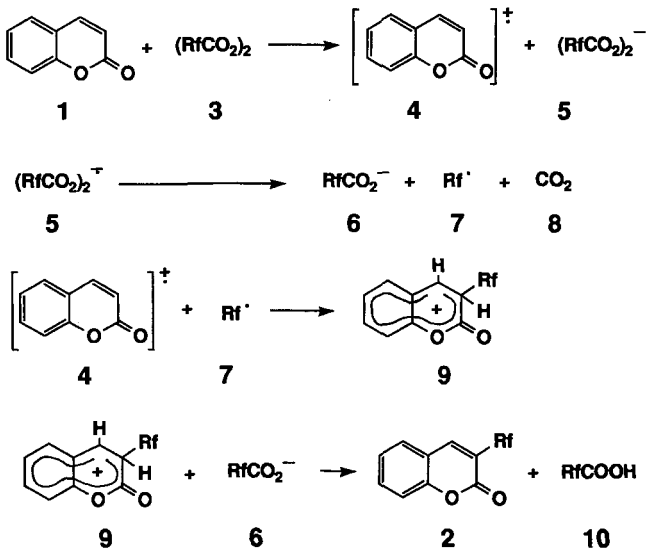
Table 2. Synthesis of 3-(perfluoroalkyl)coumarins **2**[a]

Run	Compd.	Substituents R¹	R²	R³	R⁴	R_f	Yield of **2**[b] %
1	**a**	H	H	H	H	C_3F_7	33
2	**b**	Me	H	H	H	C_3F_7	26
3	**c**	H	Me	H	H	C_3F_7	28
4	**d**	Me	H	Me	H	C_3F_7	33
5	**e**	Me	H	OH	H	C_3F_7	28
6	**f**	Me	H	OMe	H	C_3F_7	57
7	**g**	Me	H	NH_2	H	C_3F_7	trace[c]
8	**h**	Me	H	NMe_2	H	C_3F_7	35
9	**i**	Me	H	NEt_2	H	C_3F_7	36
10	**i'**[d]	Me	H	NEt_2	H	CF_3	21
11	**i''**[e]	Me	H	NEt_2	H	C_7F_{15}	29
12	**j**[f]	Me	$CH_2[CH_2]_2N[CH_2]_2CH_2$			C_3F_7	15
13	**k**	CF_3	H	OMe	H	C_3F_7	43
14	**l**	CF_3	H	NH_2	H	C_3F_7	46
15	**m**	CF_3	H	NMe_2	H	C_3F_7	39
16	**n**	CF_3	H	NEt_2	H	C_3F_7	24
17	**n'**[d]	CF_3	H	NEt_2	H	CF_3	67
18	**n''**[e]	CF_3	H	NEt_2	H	C_7F_{15}	57
19	**o**[f]	CF_3	$CH_2[CH_2]_2N[CH_2]_2CH_2$			C_3F_7	26

[a] Dichloromethane solution (40 ml) of coumarin **1** (2 mmol) refluxed with a 5.0% bis(heptafluorobutyryl) peroxide (2 mmol)/Freon 113 solution (17.0 g) under argon for 4 h. — [b] Isolated yield based on the peroxide. — [c] Identified by GC/MS. — [d] Dichloromethane solution (40 ml) of coumarin **1** (2 mmol) refluxed with a 0.71% bis(trifluoroacetyl) peroxide (2 mmol)/Freon 113 solution (63.6 g) under argon for 16 h. — [e] Dichloromethane solution (40 ml) of coumarin **1** (2 mmol) refluxed with a 4.7% bis(pentadecafluorooctanoyl) peroxide (2 mmol)/Freon 113 solution (35.1 g) under argon for 4 h. — [f] Dichloromethane solution (20 ml) of coumarin **1** (1 mmol) refluxed with a 5.0% bis(heptafluorobutyryl) peroxide (1 mmol)/Freon 113 solution (8.5 g) under argon for 4 h.

Scheme 3 shows a reasonable reaction mechanism for the regioselective perfluoroalkylation of coumarins **1**. As has been reported, a one-electron transfer from **1** to a peroxide **3** leads to a radical cation **4** and a radical anion **5**[1a]. The radical anion **5** decomposes to produce a perfluoroalkyl radical **7**, which reacts with **4** to give the most stable intermediate **9**. Deprotonation of **9** affords **2**.

Scheme 3



1 3 4 5 5 6 7 8 4 7 9 9 6 2 10

Absorption and Fluorescence Spectra of Coumarins

Table 3 summarizes the absorption and fluorescence spectral data of coumarins **1** and **2**. The absorption maxima (λ_{max}) of 3-(heptafluoropropyl)coumarins **2** show bathochromic shifts of 9–49 nm compared with the corresponding 3-unsubstituted coumarins **1**. The longest wavelength absorption band of coumarins has been assigned to a π-π* transition[4]. Bathochromic shifts of λ_{max} of coumarins caused by the introduction of electron-pushing groups into the 7-position and electron-withdrawing groups into the 3-position have been reported[5].

Table 3. Absorption and fluorescence spectra of coumarins[a]

Compd	λ_{max} (ε) nm	λ_{ex} nm	λ_{em} nm	RFI[b]
1a	273 (10900)	—[c]	—[c]	—[c]
2a	282 (13000)	—[c]	—[c]	—[c]
1b	270 (11000)	—[c]	—[c]	—[c]
2b	280 (13500)	—[c]	—[c]	—[c]
1c	275 (13300)	—[c]	—[c]	—[c]
2c	284 (16300)	—[c]	—[c]	—[c]
1d	275 (10000)	339	375	0.05
2d	287 (12000)	356	407	0.01
1e	321 (13400)	330	390	3.73
2e	339 (15300)	403	465	3.06
1f	320 (13400)	325	380	1.00
2f	336 (16500)	350	410	0.24
1h	365 (22000)	371	449	18.28
2h	394 (27400)	400	462	6.53
1i	370 (23800)	378	445	16.68
2i	400 (28800)	403	460	4.42
2i'	394 (24700)	402	462	2.77
2i''	401 (32200)	405	460	5.05
1j	388 (21000)	398	465	12.52
2j	418 (27400)	425	480	6.11
1k	332 (11100)	342	415	0.58
2k	362 (14700)	385	480	0.11
1l	380 (16800)	388	479	8.91
2l	424 (22200)	427	537	0.04
1m	394 (19000)	403	510	3.20
2m	442 (24800)	445	560	0.07
1n	400 (20800)	405	505	1.79
2n	447 (29500)	473	555	0.86
2n'	441 (24000)	455	540	0.80
2n''	447 (27300)	475	555	0.64
1o	421 (20600)	427	525	4.62
2o	470 (27800)	506	582	<0.01

[a] Measured in EtOH at 25°C. — [b] Relative fluorescence intensity (substrate: 1×10^{-6} mol dm^{-3}, **1f** = 1.00). — [c] No fluorescence was observed.

The emission maxima (λ_{em}) of **2** also show bathochromic shifts compared with the corresponding **1**. The extinction

coefficients (ε) of **2** are larger than those of **1**. No remarkable differences of λ_{max} among 3-(trifluoromethyl)-, 3-(heptafluoropropyl)-, and 3-(pentadecafluoroheptyl)coumarins are observed, suggesting similar electron-withdrawing abilities of CF_3, C_3F_7, and C_7F_{15} groups. The relative fluorescence intensities (RFI) of all 3-(perfluoroalkyl)coumarins **2** are weaker than that of the corresponding **1**.

Photostability of Coumarins

In order to evaluate the photostabilities of the coumarins, UV irradiation of an ethanol solution of the respective coumarin in a borosilicate glass in the air (200-W high-pressure mercury lamp) has been carried out. Figure 1 shows the changes in the absorption maxima of coumarins **1i**, **2i**, **2i'**, and **2i''** vs time of irradiation.

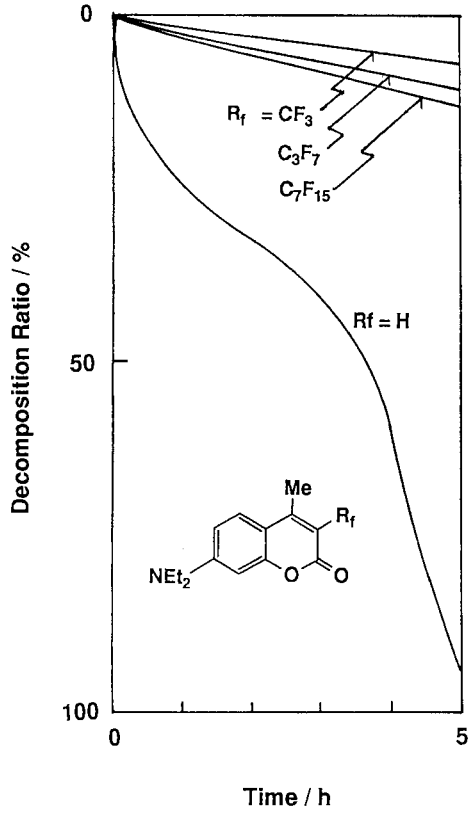


Figure 1. Irradiation of an ethanol solution (30 ml) of a coumarin **2** (0.05 mmol dm^{-3}) in a borosilicate glass tube with a 200-W high-pressure mercury lamp using a merry-go-round apparatus in the presence of air at room temperature

As expected, 3-(perfluoroalkyl)coumarins **2i**, **2i'**, and **2i''** are more stable than the 3-unsubstituted coumarin **1i**. Coumarins are known to dimerize upon UV irradiation[6]. Photodecomposition of 7-(diethylamino)-4-methylcoumarin has been shown to proceed by way of oxidation of the 4-methyl group to the carboxyl group and the 7-diethylamino group to an amino group[7]. Bulky and electron-withdrawing 3-perfluoroalkyl groups of **2** may inhibit the dimerization of coumarins and the oxidation of the 4-methyl group and lower the nucleophilicity of diethylamino nitrogen, thus suppressing the oxidation.

Conclusion

3-(Perfluoroalkyl)coumarins **2** are easily obtained in moderate yields by treatment of 3-unsubstituted coumarins **1** with bis(perfluoroalkanoyl) peroxides. The λ_{max} and λ_{em} of **2** show bathochromic shifts compared with **1**. Though the introduction of perfluoroalkyl groups into the 3-position of coumarins lowers the fluorescence intensities, the derivatives **2** are much more stable towards UV irradiation than **1**.

Experimental

Melting points: Rigaku 8085EI TG-DSC instrument. – ^{1}H-, ^{13}C-, and ^{19}F NMR: Jeol JUM-GX 270 and Hitachi R-22 spectrometers. – Mass, UV, IR, and fluorescence spectra: Shimadzu 9020 DF, Jasco UVIDEC-410, Perkin Elmer FT-IR 1640, and Hitachi 650-10S spectrometers. – Gas chromatography: Shimadzu GC-8A gas chromatograph.

Materials: Bis(perfluoroalkanoyl) peroxides were prepared as described in the literature[8]. They were not isolated and used as solutions in Freon 113. The concentrations of the peroxides were determined by iodometry. Coumarin, 6-methyl-, and 7-(diethylamino)-4-methylcoumarins (**1a**, **1c**, and **1i**) were purchased from Tokyo Kasei Co., Ltd. 2,3,6,7-Tetrahydro-9-methyl- and 2,3,6,7-tetrahydro-9-(trifluoromethyl)-1*H*,5*H*,11*H*-pyrano[2',3'-4,5]benzo[1,2,3-ij]quinolizin-11-ones (**1j**, **1o**), 7-amino-3-methyl-, and 7-(diethylamino)-3-(1-methyl-2-benzimidazolyl)coumarin (**1g**, **1q**) were obtained from Eastman Kodak Co. The other coumarins were synthesized by treatment of ethyl aceto- and 4,4,4-trifluoroacetoacetates with the corresponding phenols.

Reaction of Coumarin (**1a**) *with Bis(heptafluorobutyryl) Peroxide:* To a dichloromethane solution (20 ml) of **1a** was added a 5.0% bis(heptafluorobutyryl) peroxide/Freon 113 solution (8.5 g, 1.0 mmol). After completion of the reaction, the products were analyzed gas chromatographically [injection temperature: 150°C, detector temperature: 150°C, column temperature: 110°C, column: 20% Silicone KF-96 on Uniport B (60–80 mesh), 3 mm × 1 m, glass, flow: N_2, 30 ml min^{-1}].

Synthesis of 3-(Perfluoroalkyl)coumarins **2**: According to the general procedure, to a dichloromethane solution (40 ml) of coumarin **1** (2.0 mmol) was added a bis(perfluoroalkanoyl) peroxide/Freon 113 solution (2.0 mmol). The mixture was refluxed under argon for 4 h. After the reaction was complete, the organic layer containing the products was washed with brine (40 ml), a 10% aqueous sodium hydrogencarbonate solution (40 ml), and brine (40 ml). The organic layer was dried with sodium sulfate. After evaporation of the solvent, the crude product was isolated by column chromatography (SiO_2, CH_2Cl_2) and recrystallized from ethanol or hexane. The physical and spectral data of 3-(perfluoroalkyl)coumarins **2** are listed below.

3-(Heptafluoropropyl)coumarin (**2a**): M.p. 73°C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 7.37–7.42 (m, 2H), 7.64–7.73 (m, 2H), 8.16 (s, 1H). – MS (EI, 70 eV): *m/z* (%) = 314 (39) [M^+], 195 (100). – IR (KBr): $\tilde{\nu}$ = 1744 cm^{-1}.

$C_{12}H_5F_7O_2$ (314.2) Calcd. C 45.88 H 1.60
Found C 45.61 H 1.45

3-(Heptafluoropropyl)-4-methylcoumarin (**2b**): M.p. 111°C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 2.68 (s, 3H), 7.36 (dd, *J* = 8.8, 1.4 Hz, 1H), 7.38 (ddd, *J* = 8.8, 8.8, 1.4 Hz, 1H), 7.66 (ddd, *J* = 8.8, 8.8, 1.4 Hz, 1H), 7.83 (dd, *J* = 8.8, 1.4 Hz, 1H). – MS (EI,

70 eV): *m/z* (%) = 328 (44) [M$^+$], 209 (100). – IR (KBr): $\tilde{\nu}$ = 1728 cm^{-1}.

$C_{13}H_7F_7O_2$ (328.2) Calcd. C 47.58 H 2.15
Found C 47.68 H 2.38

3-(Heptafluoropropyl)-6-methylcoumarin (**2c**): M.p. 111°C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 2.44 (s, 3H), 7.28 (d, *J* = 8.6 Hz, 1H), 7.48 (s, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 8.08 (s, 1H). – MS (EI, 70 eV): *m/z* (%) = 328 (40) [M$^+$], 209 (100). – IR (KBr): $\tilde{\nu}$ = 1733 cm^{-1}.

$C_{13}H_7F_7O_2$ (328.2) Calcd. C 47.58 H 2.15
Found C 47.35 H 2.11

3-(Heptafluoropropyl)-4,7-dimethylcoumarin (**2d**): M.p. 119°C (ethanol). – ^{1}H NMR ($CDCl_3$): δ = 2.48 (s, 3H), 2.64 (s, 3H), 7.14 (s, 1H), 7.18 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H). – MS (EI, 70 eV): *m/z* (%) = 342 (34) [M$^+$], 223 (100). – IR (KBr): $\tilde{\nu}$ = 1733 cm^{-1}.

$C_{14}H_9F_7O_2$ (342.2) Calcd. C 49.14 H 2.65
Found C 49.08 H 2.58

3-(Heptafluoropropyl)-7-hydroxy-4-methylcoumarin (**2e**): M.p. 151°C (ethanol). – ^{1}H NMR ($CDCl_3$): δ = 2.63 (s, 3H), 6.94 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.98 (d, *J* = 2.4 Hz, 1H), 7.70 (d, *J* = 9.2 Hz, 1H), 7.80 (br s, 1H). – MS (EI, 70 eV): *m/z* (%) = 344 (53) [M$^+$], 225 (100). – IR (KBr): $\tilde{\nu}$ = 3389, 1706 cm^{-1}.

$C_{13}H_7F_7O_3$ (344.2) Calcd. C 45.36 H 2.05
Found C 45.57 H 2.00

3-(Heptafluoropropyl)-7-methoxy-4-methylcoumarin (**2f**): M.p. 143°C (ethanol). – ^{1}H NMR ($CDCl_3$): δ = 2.62 (s, 3H), 3.91 (s, 3H), 6.80 (d, *J* = 3.1 Hz, 1H), 6.92 (dd, *J* = 9.2, 3.1 Hz, 1H), 7.71 (d, *J* = 9.2 Hz, 1H). – MS (EI, 70 eV): *m/z* (%) = 358 (42) [M$^+$], 239 (100). – IR (KBr): $\tilde{\nu}$ = 1733 cm^{-1}.

$C_{14}H_9F_7O_3$ (358.2) Calcd. C 46.94 H 2.53
Found C 47.12 H 2.39

7-(Dimethylamino)-3-(heptafluoropropyl)-4-methylcoumarin (**2h**): M.p. 147°C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 2.55 (s, 3H), 3.10 (s, 6H), 6.46 (d, *J* = 3.1 Hz, 1H), 6.66 (dd, *J* = 9.1, 3.1 Hz, 1H), 7.59 (d, *J* = 9.1 Hz, 1H). – MS (EI, 70 eV): *m/z* (%) = 371 (50) [M$^+$], 252 (100). – IR (KBr): $\tilde{\nu}$ = 1722 cm^{-1}.

$C_{15}H_{12}F_7NO_2$ (371.3)
Calcd. C 48.53 H 3.26 N 3.77
Found C 48.40 H 3.16 N 3.74

7-(Diethylamino)-3-(heptafluoropropyl)-4-methylcoumarin (**2i**): M.p. 113°C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 1.22 (t, 6H), 2.53 (s, 3H), 3.44 (q, 4H), 6.44 (d, *J* = 2.5 Hz, 1H), 6.63 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 12.1, 15.6, 44.7, 96.3, 105.7, 108.1, 109.3, 115.9, 116.1, 118.1, 127.2, 152.1, 155.9, 157.2, 157.4. – ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H): δ = −1.6 (t), −24.1 (q), −46.4 (t). – MS (EI, 70 eV): *m/z* (%) = 399 (35) [M$^+$], 384 (100). – IR (KBr): $\tilde{\nu}$ = 1724, 1347, 1235 cm^{-1}.

$C_{17}H_{16}F_7NO_2$ (399.3)
Calcd. C 51.14 H 4.04 N 3.51
Found C 51.13 H 4.14 N 3.47

7-(Diethylamino)-4-methyl-3-(trifluoromethyl)coumarin (**2i'**): M.p. 95°C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 1.23 (t, *J* = 9.2 Hz, 6H), 2.55 (t, *J* = 2.4 Hz, 3H), 3.43 (q, *J* = 7.3 Hz, 4H), 6.45 (d, *J* = 2.5 Hz, 1H), 6.63 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.56 (d, *J* = 9.2 Hz, 1H). – MS (EI, 70 eV): *m/z* (%) = 299 (33) [M$^+$], 284 (100). – IR (KBr): $\tilde{\nu}$ = 1722 cm^{-1}.

$C_{15}H_{16}F_3NO_2$ (299.3)
Calcd. C 60.20 H 5.39 N 4.68
Found C 60.09 H 5.00 N 4.61

7-(Diethylamino)-4-methyl-3-(pentadecafluoroheptyl)coumarin (**2i''**): M.p. 131°C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 1.23 (t, *J* = 7.1 Hz, 6H), 2.54 (t, *J* = 2.8 Hz, 3H), 3.44 (q, *J* = 7.1 Hz, 4H), 6.47 (d, *J* = 2.6 Hz, 1H), 6.65 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.58 (d, *J* = 9.2 Hz, 1H). – MS (EI, 70 eV): *m/z* (%) = 599 (23) [M$^+$], 584 (51), 280 (100). – IR (KBr): $\tilde{\nu}$ = 1719 cm^{-1}.

$C_{21}H_{16}F_{15}NO_2$ (599.3)
Calcd. C 42.09 H 2.69 N 2.34
Found C 41.94 H 2.49 N 2.42

10-(Heptafluoropropyl)-2,3,6,7-tetrahydro-9-methyl-1H,5H,11H-pyrano[2',3'-4,5]benzo[1,2,3-ij]quinolizine-11-one (**2j**): M.p. 178°C (ethanol). – ^{1}H NMR ($CDCl_3$): δ = 1.96 (quint, *J* = 6.1 Hz, 4H), 2.80 (t, *J* = 6.1 Hz, 2H), 2.86 (t, *J* = 6.1 Hz, 2H), 3.30 (t, *J* = 6.1 Hz, 2H), 3.32 (t, *J* = 6.1 Hz, 2H), 7.16 (s, 1H). – MS (EI, 70 eV): *m/z* (%) = 423 (83) [M$^+$], 304 (100). – IR (KBr): $\tilde{\nu}$ = 1713 cm^{-1}.

$C_{19}H_{16}F_7NO_2$ (423.3)
Calcd. C 53.91 H 3.80 N 3.31
Found C 53.87 H 3.65 N 3.51

3-(Heptafluoropropyl)-7-methoxy-4-(trifluoromethyl)coumarin (**2k**): M.p. 94°C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 3.94 (s, 3H), 6.87 (d, *J* = 3.0 Hz, 1H), 6.96 (dd, *J* = 9.4, 3.0 Hz, 1H), 7.81 (dq, *J* = 9.4, 2.4 Hz, 1H). – MS (EI, 70 eV): *m/z* (%) = 412 (35) [M$^+$], 293 (100), 265 (85). – IR (KBr): $\tilde{\nu}$ = 1737 cm^{-1}.

$C_{14}H_6F_{10}O_3$ (412.2) Calcd. C 40.80 H 1.47
Found C 41.00 H 1.46

7-Amino-3-(heptafluoropropyl)-4-(trifluoromethyl)coumarin (**2l**): M.p. 209°C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 4.61 (br, 2H), 6.60 (d, *J* = 2.4 Hz, 1H), 6.63 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.67 (dq, *J* = 9.2, 2.7 Hz, 1H). – MS (EI, 70 eV): *m/z* (%) = 397 (41) [M$^+$], 278 (100). – IR (KBr): $\tilde{\nu}$ = 3467, 3367, 1706 cm^{-1}.

$C_{13}H_5F_{10}NO_2$ (397.2)
Calcd. C 39.31 H 1.27 N 3.53
Found C 39.23 H 1.34 N 3.60

7-(Dimethylamino)-3-(heptafluoropropyl)-4-(trifluoromethyl)-coumarin (**2m**): M.p. 147°C (ethanol). – ^{1}H NMR ($CDCl_3$): δ = 3.14 (s, 6H), 6.48 (d, *J* = 2.4 Hz, 1H), 6.68 (dd, *J* = 9.8, 2.4 Hz, 1H), 7.67 (dq, *J* = 9.8, 2.4 Hz, 1H). – MS (EI, 70 eV): *m/z* (%) = 425 (82) [M$^+$], 307 (100), 278 (42). – IR (KBr): $\tilde{\nu}$ = 1722 cm^{-1}.

$C_{15}H_9F_{10}NO_2$ (425.2)
Calcd. C 42.37 H 2.13 N 3.29
Found C 42.25 H 1.96 N 3.42

7-(Diethylamino)-3-(heptafluoropropyl)-4-(trifluoromethyl)coumarin (**2n**): M.p. 119°C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 1.25 (t, *J* = 7.0 Hz, 6H), 3.47 (q, *J* = 7.0 Hz, 4H), 6.48 (d, *J* = 2.9 Hz, 1H), 6.66 (dd, *J* = 9.5, 2.9 Hz, 1H), 7.66 (dq, *J* = 9.5, 2.5 Hz, 1H). – MS (EI, 70 eV): *m/z* (%) = 453 (37) [M$^+$], 438 (100). – IR (KBr): $\tilde{\nu}$ = 1722 cm^{-1}.

$C_{17}H_{13}F_{10}NO_2$ (453.3)
Calcd. C 45.05 H 2.89 N 3.09
Found C 44.95 H 2.91 N 3.25

7-(Diethylamino)-3,4-bis(trifluoromethyl)coumarin (**2n'**): M.p. 142°C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 1.25 (t, *J* = 7.3 Hz, 6H), 3.47 (q, *J* = 7.3 Hz, 4H), 6.49 (d, *J* = 2.7 Hz, 1H), 6.66 (dd, *J* = 9.4, 2.7 Hz, 1H), 7.66 (dq, *J* = 9.4, 2.4 Hz, 1H). – MS (EI, 70 eV): *m/z* (%) = 353 (34) [M$^+$], 338 (100). – IR (KBr): $\tilde{\nu}$ = 1728 cm^{-1}.

$C_{15}H_{13}F_6NO_2$ (353.3)
Calcd. C 51.00 H 3.71 N 3.97
Found C 51.38 H 3.58 N 4.01

7-(Diethylamino)-3-(pentadecafluoroheptyl)-4-(trifluoromethyl)-coumarin (**2n''**): M.p. 108 °C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 1.25 (t, *J* = 7.2 Hz, 6H), 3.47 (q, *J* = 7.2 Hz, 4H), 6.49 (d, *J* = 2.6 Hz, 1H), 6.66 (dd, *J* = 9.8, 2.6 Hz, 1H), 7.66 (dq, *J* = 9.8, 2.6 Hz, 1H). – MS (EI, 70 eV): *m/z* (%) = 653 (33) [M^+], 638 (83), 335 (100). – IR (KBr): $\tilde{\nu}$ = 1736 cm^{-1}.

$C_{21}H_{13}F_{18}NO_2$ (653.3)
Calcd. C 38.61 H 2.01 N 2.14
Found C 38.36 H 1.84 N 2.41

10-(Heptafluoropropyl)-2,3,6,7-tetrahydro-9-(trifluoromethyl)-1H,5H,11H-pyrano[2',3':4,5]benzo[1,2,3-ij]quinolizin-11-one (**2o**): M.p. 161 °C (ethanol). – ^{1}H NMR ($CDCl_3$): δ = 1.98 (m, 4H), 2.78 (t, *J* = 6.1 Hz, 2H), 2.85 (t, *J* = 6.1 Hz, 2H), 3.35 (t, *J* = 6.1 Hz, 2H), 3.37 (t, *J* = 6.1 Hz, 2H), 7.25 (s, 1H). – MS (EI, 70 eV): *m/z* (%) = 477 (52) [M^+], 358 (100). – IR (KBr): $\tilde{\nu}$ = 1722 cm^{-1}.

$C_{19}H_{13}F_{10}NO_2$ (477.3)
Calcd. C 47.81 H 2.75 N 2.93
Found C 47.91 H 2.76 N 2.80

Photostability of Coumarins: An ethanol solution (30 ml) of coumarin (0.05 mmol dm^{-3}) in a borosilicate glass was irradiated with a 200-W high-pressure mercury lamp by using a merry-go-round apparatus in the presence of air at room temp. The decomposition ratio was calculated on the basis of the changes of the absorbance at λ_{max} of the solution by irradiation [$(A_0 - A_t)/A_0$; A_0: absorbance at 0 h, A_t: absorbance at *t* h].

CAS Registry Numbers

1a: 91-64-5 / **1b**: 607-71-6 / **1c**: 92-48-8 / **1d**: 14002-90-5 / **1e**: 90-33-5 / **1f**: 2555-28-4 / **1g**: 26093-31-2 / **1h**: 87-01-4 / **1i**: 91-44-1 / **1j**: 41267-76-9 / **1k**: 575-04-2 / **1l**: 53518-15-3 / **1m**: 53518-14-2 / **1n**: 41934-47-8 / **1o**: 53518-18-6 / **2a**: 133721-24-1 / **2b**: 137516-22-4 / **2c**: 137516-23-5 / **2d**: 133721-25-2 / **2e**: 137516-24-6 / **2f**: 133721-26-3 / **2h**: 133721-27-4 / **2i**: 133721-28-5 / **2i'**: 133721-29-6 / **2i''**: 133721-30-9 / **2j**: 137516-25-7 / **2k**: 133721-31-0 / **2l**: 137516-26-8 / **2m**: 133721-32-1 / **2n**: 133721-33-2 / **2n'**: 133721-34-3 / **2n''**: 137516-27-9 / **2o**: 137516-28-0

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